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APPLICATION OF A SPRAY DEPOSITION METHOD FOR REVERSED PHASE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

by

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Four coal gasification wastewater samples were analyzed for nonvolatile and polar organics by liquid chromatography-mass spectrometry (LC/MS). Samples were separated on a reverse phase liquid chromatographic column using an aqueous solvent as the eluant. A special spray deposition device was constructed to spray the LC effluent as an aerosol on a Finnigan moving belt LC/MS interface. The evaporated solute on the belt was fed directly to an MS for spectral analysis.

In addition to several common organics such as phenol, guaiacol, methyl and dimethyl phenols, seven polar compounds were found, and the mass spectrum of each of these was obtained. They could not be identified, however, using available literature or data bases.

The LC aerosol deposition device constructed for the study shows good potential for intruducing aqueous eluants on a moving belt LC/MS interface.

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Analytical Chemistry Branch characterizes chemical constituents of water and soil.

An essential step in determining transport and fate of organic pollutants is the complex procedure of analyzing industrial and environmental wastes. Gas chromatography-mass spectrometry is widely used for the analysis of volatile compounds. This report describes a study of the use of liquid chromatography-mass spectrometry for the analysis of wastewater samples for polar or low volatility organics. The study included the evaluation of a special spray deposition device.

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ABSTRACT

Four coal gasification wastewater samples were analyzed for non-volatile and polar organics by liquid chromatography/mass spectrometry (LC/MS). Samples were separated on a reverse phase liquid chromatographic column using an aqueous solvent as the eluant. A special spray deposition device was constructed to spray the LC effluent as an aerosol onto a Finnigan moving belt LC/MS interface; the evaporated solute on the belt was fed directly to the MS for spectral analysis.

In addition to several common organics such as phenol, guaiacol, methyl and dimethyl phenols, seven polar compounds were found; the mass spectrum of each of these was obtained. They could not be identified, however, using available literature or data bases.

The LC aerosol deposition device constructed shows good potential for introducing aqueous eluants onto a moving belt LC/MS interface.

This report covers a period from November 1982 to October 1983 and work was completed as of October 1983.

INTRODUCTION

The analysis of industrial and environmental wastes for organic pollutants is complex due to the wide polarity range of organic compounds. It is, however, an essential step in determining transport and fate of pollutants. Volatile, non-polar compounds can be extracted and analyzed by gas chromatography-mass spectrometry (GC/MS). Many polar or low volatility organics, however, are not directly amenable to extraction or GC analysis. Liquid chromatography (LC) combined with mass spectrometry (MS) offers a technique for the analysis of complex mixtures of non-volatile and polar organics.

The Finnigan LC/MS interface deposits the LC effluent directly onto a moving belt. The solvent is evaporated and the remaining solute is introduced into the MS source. Usually no problems occur when normal phase chromatography is performed. At flow rates of less than 1 milliliter per minute (ml/min) the organic solvent is easily evaporated off the belt by an infrared heater that is part of the interface. Problems occur with reverse phase chromatography, however, when the solvent system contains a high percentage of water. Most polar compounds are separated and elute in the high water content fraction during a chromatography run. When deposited on the belt, the water evaporates slowly and will "bead-up" causing sharp pressure fluctuations in the MS ion source. To aid in the evaporation of aqueous solvents and prevent "beading" on the belt, a device was constructed to spray the LC effluent as an aerosol on the belt. The spray deposition method uses heated nitrogen gas flowing through a glass tube to form an aerosol spray with the solvent; it was adapted from the description by Smith and Johnson[1] and Karger and Vouros[2].

THE AEROSOL DEVICE

Figure 1 shows the aerosol device. The spray tip is made from 1/16 in. OD, 0.01 in. ID stainless steel tubing with a 1/4 in. long tapered point (sanded and polished around the opening). The outer glass tubing is 1/4 in. OD pyrex drawn to a short taper; the opening (ground with a sanding disk) is about 2 mm in diameter. The stainless steel tube extends through the glass tube and is flush with the end.

The device is mounted on the aluminum block of the Finnigan LC/MS interface by drilling a threaded mounting hole at an angle of 40 degrees from the vertical, behind the standard hole and centered over the belt.

Nitrogen gas is heated with a Hotwatt gas heater set at 185°C. An additional heater, a 2-ft. heating tape, is wrapped tightly around the connection between the gas heater and the interface block. The temperature of the tape, controlled by a variable autotransformer, is set at about 185°C.

The sprayer tip is positioned about 1/2 in. above the belt. The 1/16 in. stainless steel tip is adjusted in the glass housing unit until a uniform spray is deposited on the belt. The nitrogen pressure required for a good aerosol is 8 to 14 psi for aqueous solvents (solvent flow rate 0.7 ml/min).

INSTRUMENTAL CONDITIONS

Liquid chromatography separations were performed on a Waters Associates 204 liquid chromatograph equipped with two Model 6000 pumps, a Model 660 solvent programmer, and a 254-nanometer ultraviolet absorbance detector. The LC effluent from the absorbance detector was was fed directly to the deposition sprayer onto the Kapton-belt-transport Finnigan LC/MS interface. The belt introduces the sample into a Finnigan 3200 Mass Spectrometer. EI ionization (70eV) or CI ionization (120eV) may be used. The initial source temperature was 60°C for both EI and CI, and the interface vaporizer was 165°C. The mass spectrometer was interfaced to a System 150 data system for acquisition and evaluation of data.

In the Finnigan LC/MS interface chamber, the solvent deposited on the belt is partially evaporated under an infrared heater and then mostly removed through two differentially pumped vacuum locks before the residue is introduced into the ion source. Operating pressure in the mass spectrometer source is generally 10^{-5} to 10^{-6} Torr. If the solvent on the belt is not evaporated by the infrared heater and the two vacuum ports, erratic sharp pressure fluctuations between 10^{-5} and 10^{-4} Torr occur that cause noise that obscures signals of interest.

Environmental effluent samples contain a complex mixture of organics that are of varying polarity. A 4.6-mm-ID x 25-cm-long Supelcosil LC-8 reverse phase LC column was chosen as it produces a good separation of compounds from moderate to high polarity. The mobile phase was 10% acetonitrile/90% water + 0.2% acetic acid held for 6 minutes, gradient to 60% acetonitrile/40% water + 0.2% acetic acid over 20 minutes. Flow rate was 0.7 ml/min. Injection volumes were 15 to 40 microliters depending on the sample.

The optimum flow rate for good resolution for this column using a gradient of water to acetonitrile is about 0.7 to 1.5 ml/min; 0.7 ml/min was the maximum flow that could be used with the aerosol spray. With the spray tip about 1/2 in. from the 3-mm-wide belt, a fine spray about 12 mm in diameter formed about the belt, resulting in about 40-80% being lost off the belt. The nitrogen gas temperature was around 185°C (measured inside the gas heater). The interface infrared heaters were turned to the maximum.

ANALYSIS OF COAL GASIFICATION WASTEWATERS

This system was used to analyze four wastewater samples provided by Pittsburgh Energy Technology Center, Pittsburgh, PA. These samples were a series of experimental wastewaters followed through a wastewater treatment procedure:

1. Ammonia stripped -- a coal gasification wastewater purged with ammonia.
2. Raffinate -- liquid left after extraction with methyl isobutyl ketone (MIK).
3. Influent -- to a biological treatment process.
4. Effluent -- from a biological process.

The ammonia stripped sample and the raffinate sample were dark brown in color and contained a dark brown sediment. Both had an aromatic odor. The influent and the effluent were both amber in color and each had a faint aromatic odor.

RESULTS AND DISCUSSION

The LC-MS chromatograms (total ion current) are shown in Figure 2. The only compounds identified were phenol, guaiacol, two methyl phenols and three dimethyl phenols. No attempt was made to identify the exact isomers of the substituted phenols. The compounds were identified by matching spectra in the National Bureau of Standards library of standard spectra and comparing to reference compounds available. Seven chromatographic peaks were unidentified. Their spectra are shown in Figures 3-6. These could not be identified using available literature or data bases.

The ammonia stripped wastewater sample was the most concentrated and contained the most compounds. As the wastewater progressed further through the treatment process, the phenolic compounds gradually disappeared. The seven unknown peaks were essentially unchanged, however. These peaks are very polar and some are apparently homologs of each other. Additional techniques, such as Fourier transform infrared spectrometry or high resolution mass spectrometry are planned for future work. These techniques are needed for positive identification.

LIMITATIONS

There are some trade-offs for this technique:

- A high nitrogen pressure is needed for a good aerosol when using an LC flow rate of 0.7 ml/min (80-100% water). This causes spray splattering off the belt, and about 40-80% of the effluent is lost. Solvent flow rates higher than 0.7 ml/min cause erratic MS pressure fluctuations. New LC micro columns (now being introduced)

that use optimum flow rates of 0.1 ml/min should minimize this problem.

- It is necessary to turn the infrared heater of the interface to maximum temperature to evaporate the finely spread aqueous drops deposited on the belt. This may decompose heat-labile compounds.

CONCLUSIONS

The LC aerosol deposition device constructed for the Finnigan moving belt interface shows good potential for the LC/MS analysis of aqueous effluent and has been demonstrated on an environmental sample. Unknown environmental effluents contain a wide polarity range of organic compounds. The best resolution and separation of these organics are done using a reverse phase column and an aqueous gradient solvent system. Future work with the new micro LC columns using lower solvent flow rates may make LC/MS analytical procedures as commonly used as GC/MS analysis.

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2. Hayes, M. J.; Lankmayer, E. P.; Vouros, P.; Karger, B. L.; McGuire, J. M., Moving Belt Interface with Spray Deposition for Liquid Chromatography/Mass Spectrometry, Anal. Chem. 1983, 55, 1745-1752.

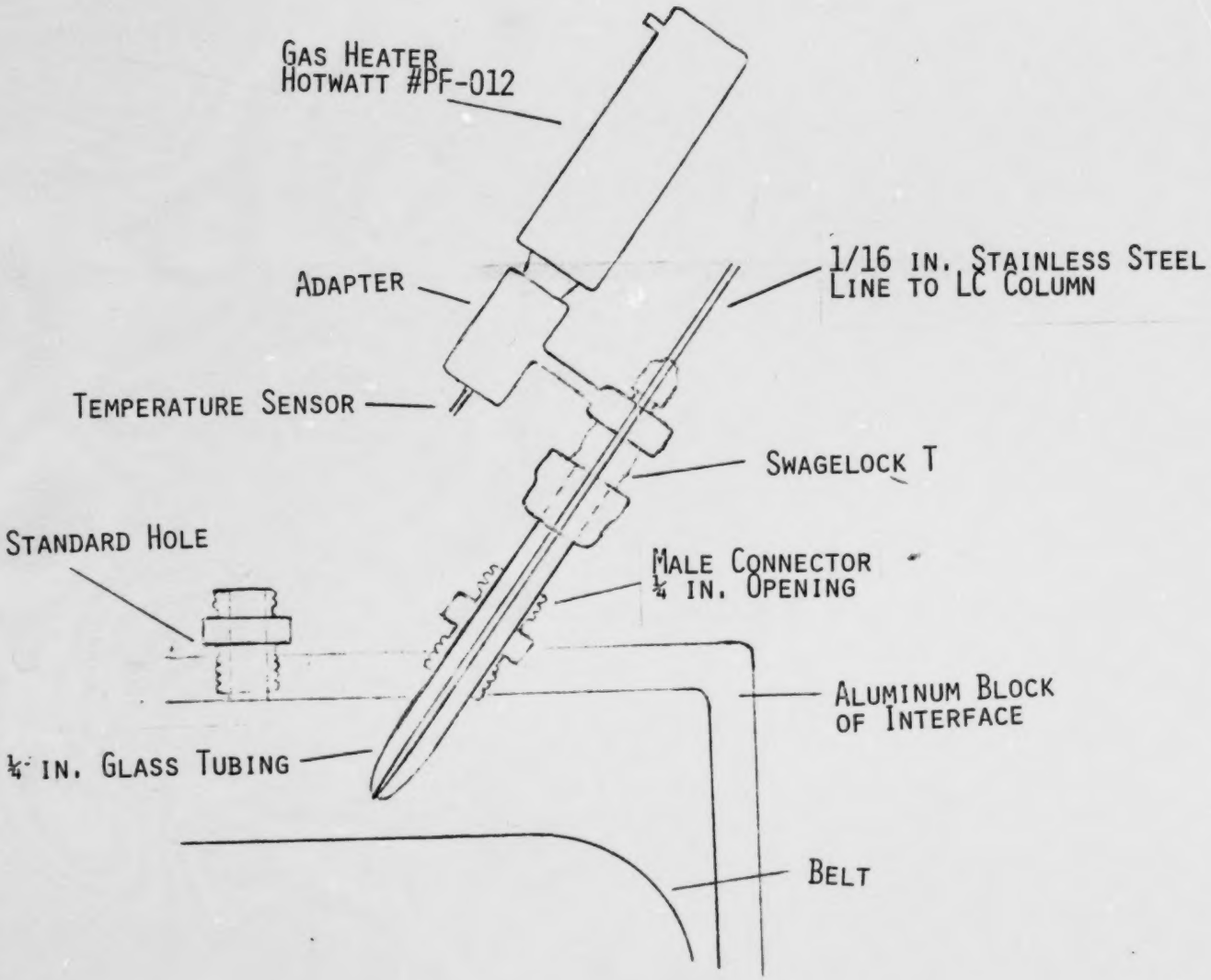

Figure 1. Diagram of Spray Deposition Device.

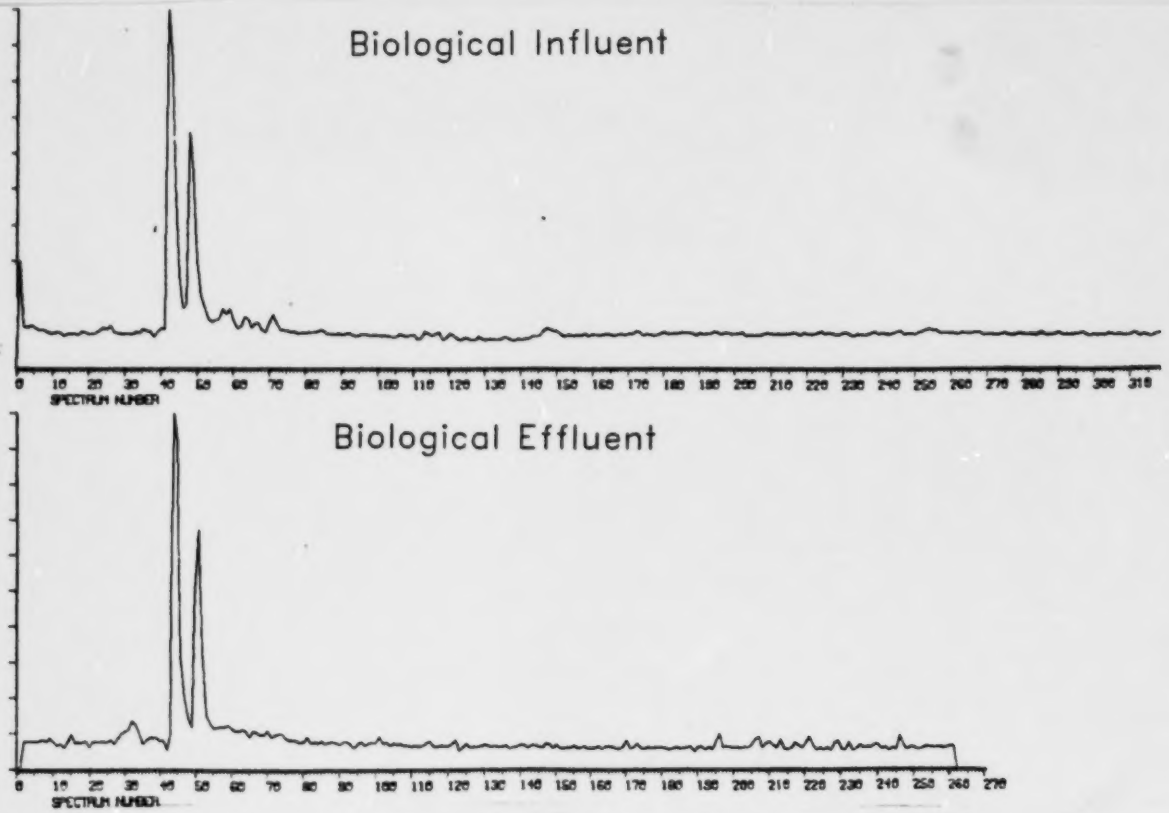

Figure 2. LC chromatograms (total ion current) of wastewater samples.

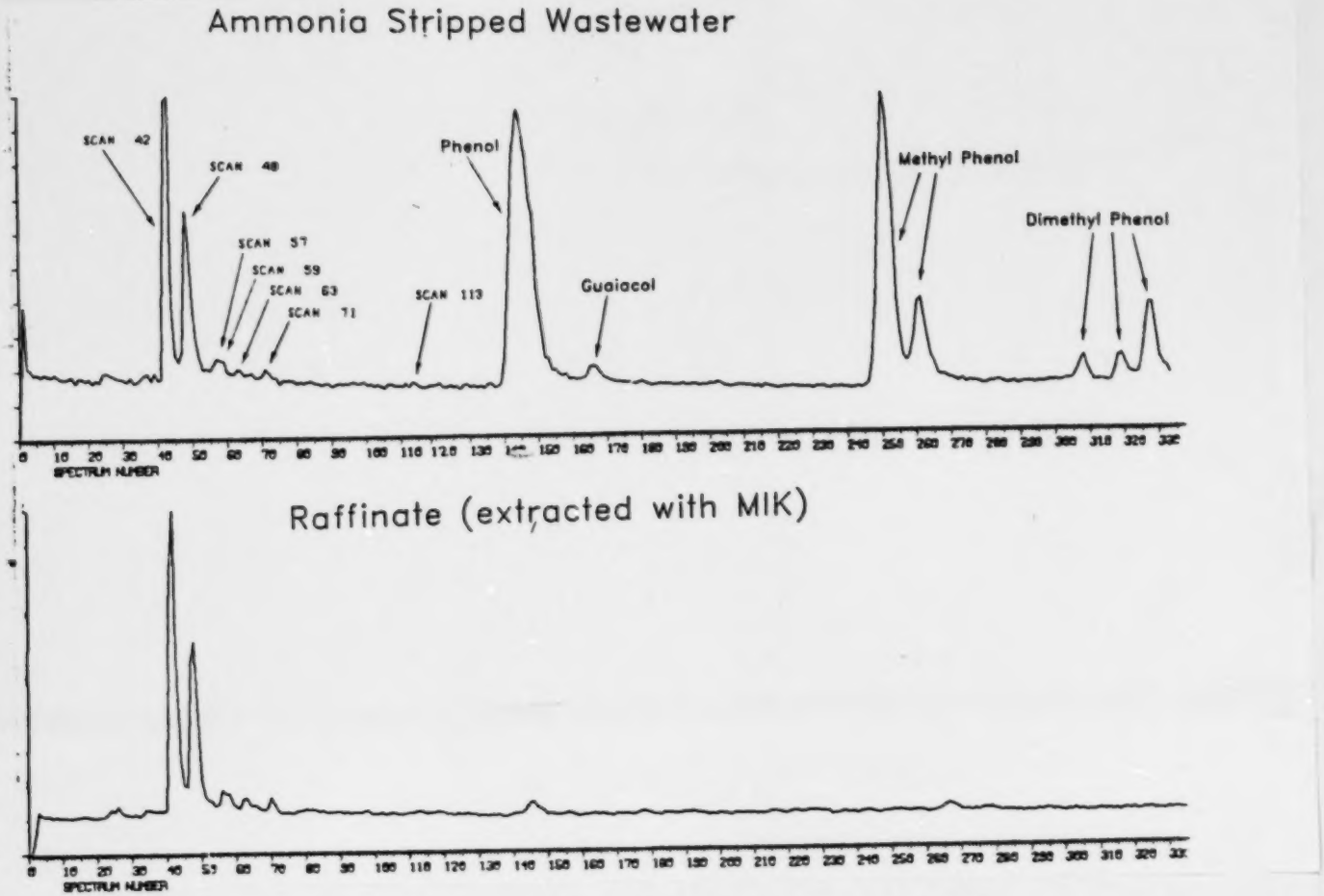

Figure 2. (Cont'd). LC chromatograms (total ion current) of wastewater samples.

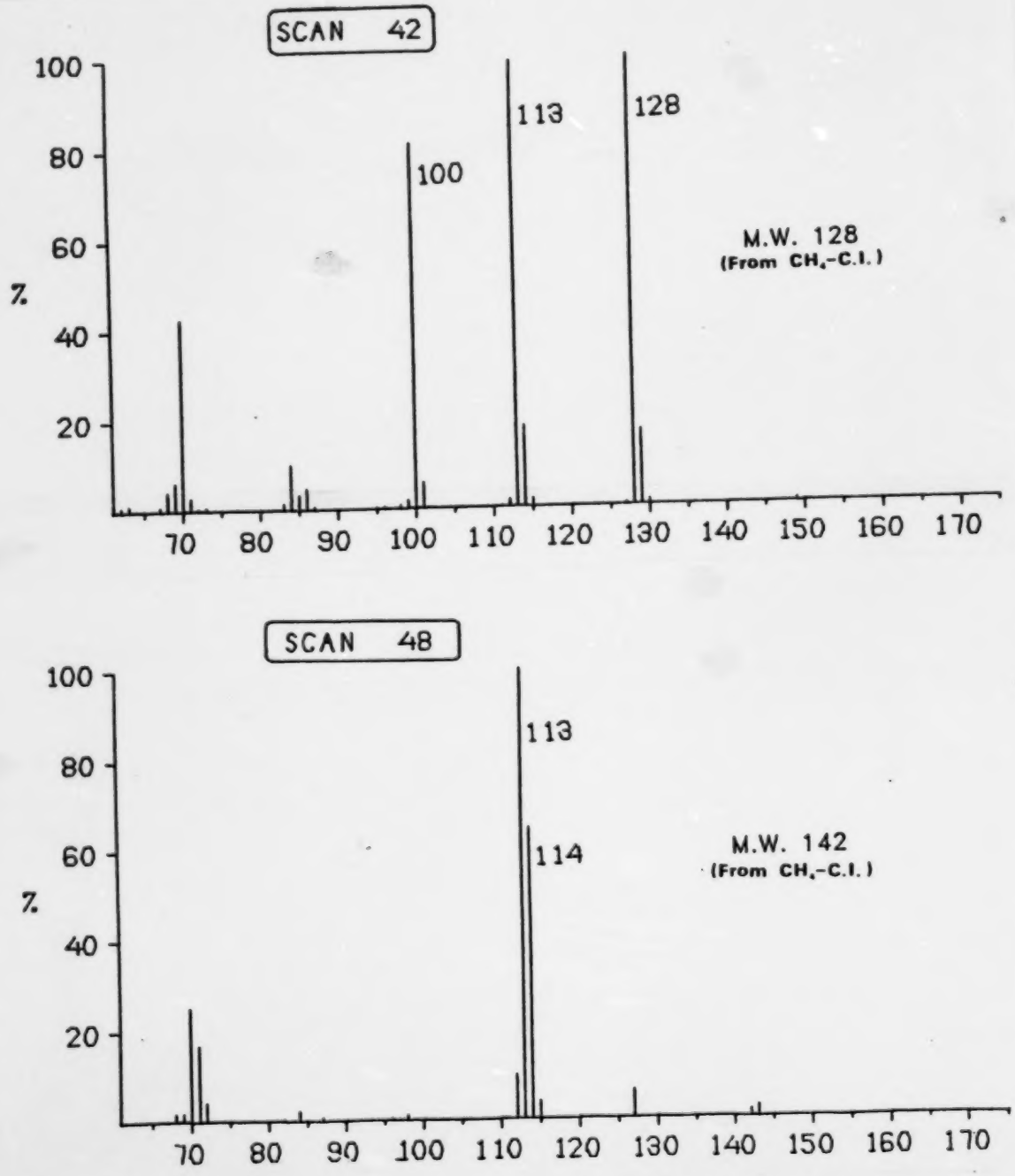

Figure 3. Electron impact mass spectra of Scan 42 and Scan 48.

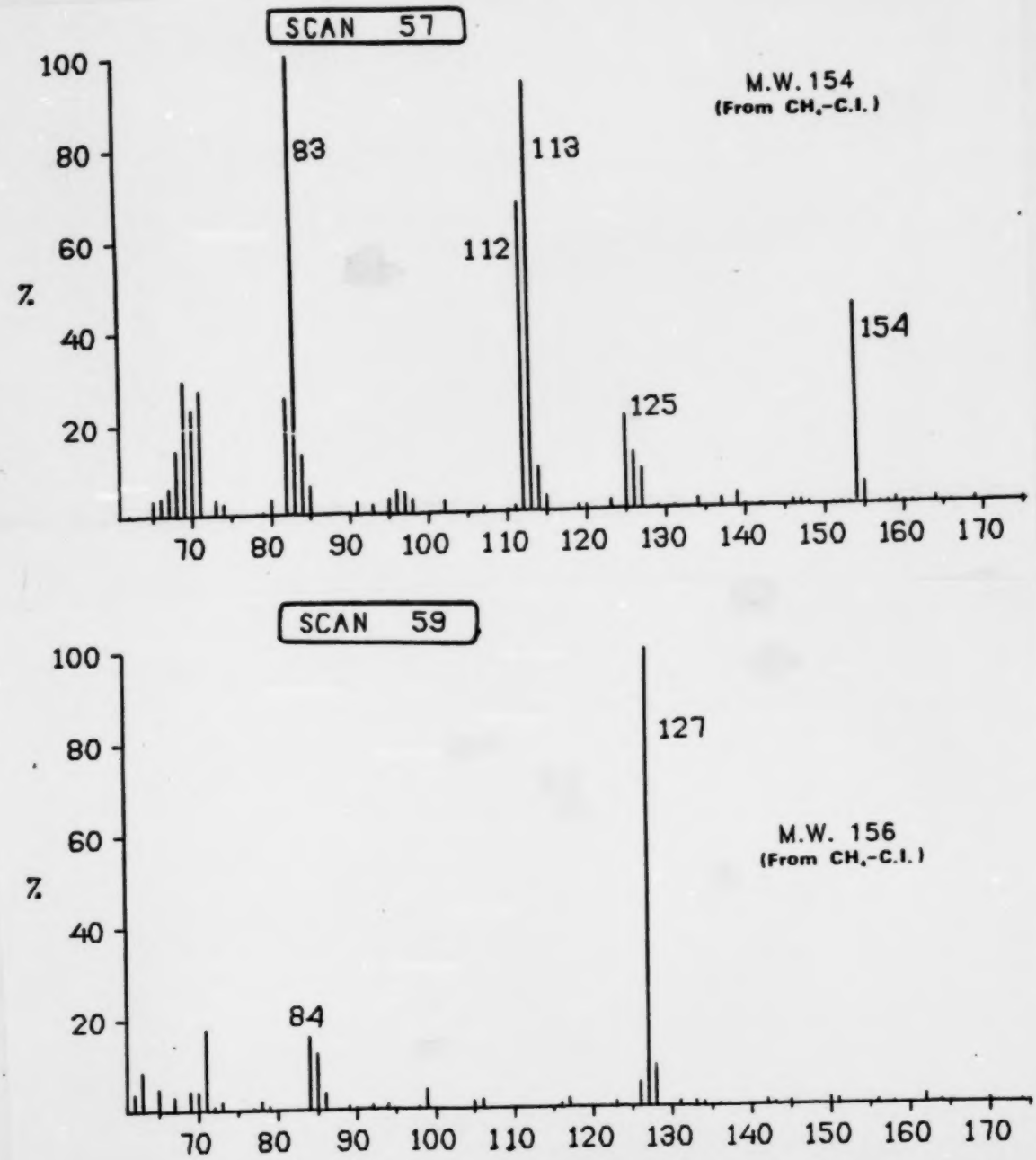

Figure 4. Electron impact mass spectra of Scan 57 and Scan 59.

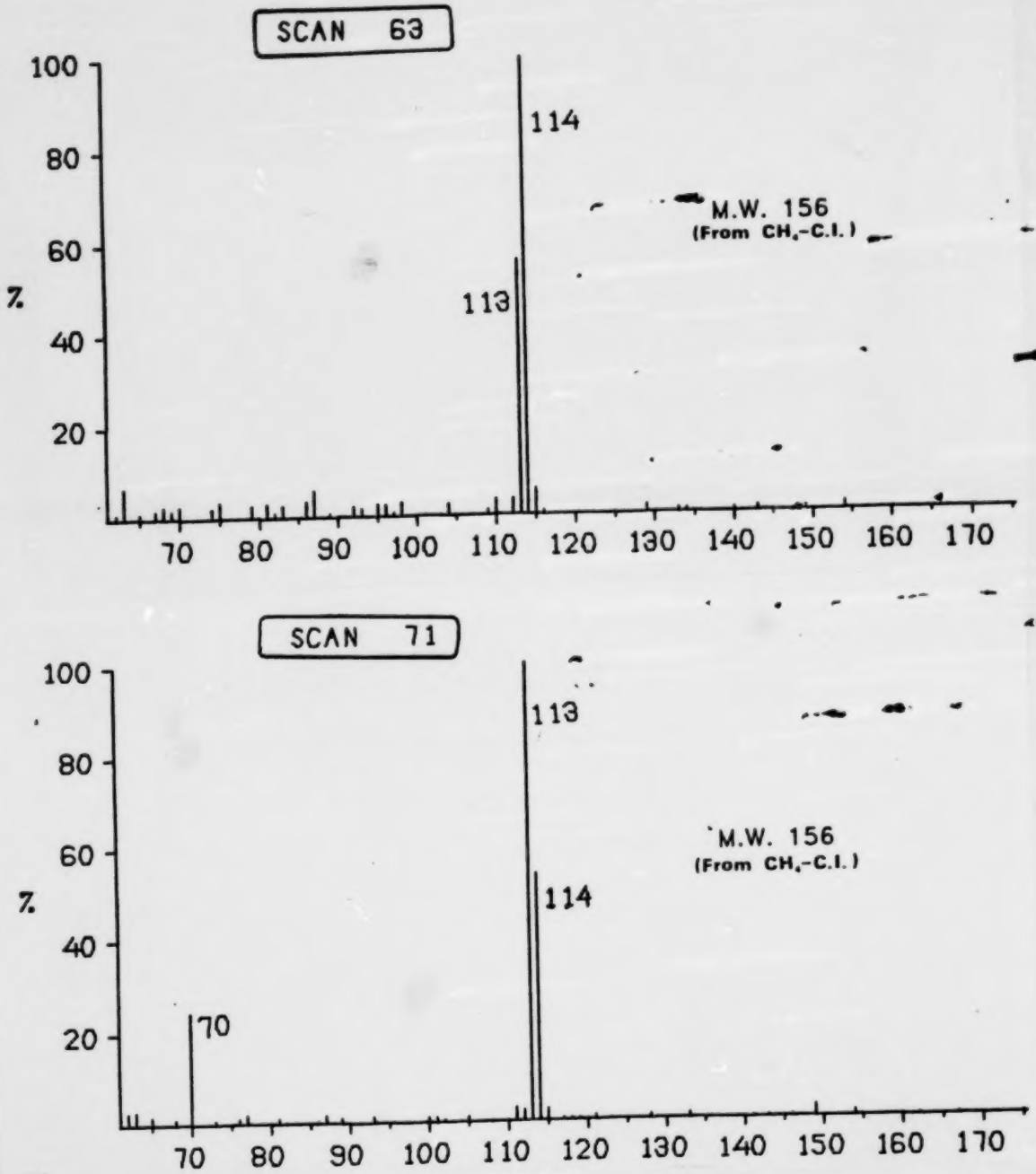

Figure 5. Electron impact mass spectra of Scan 63 and Scan 71.

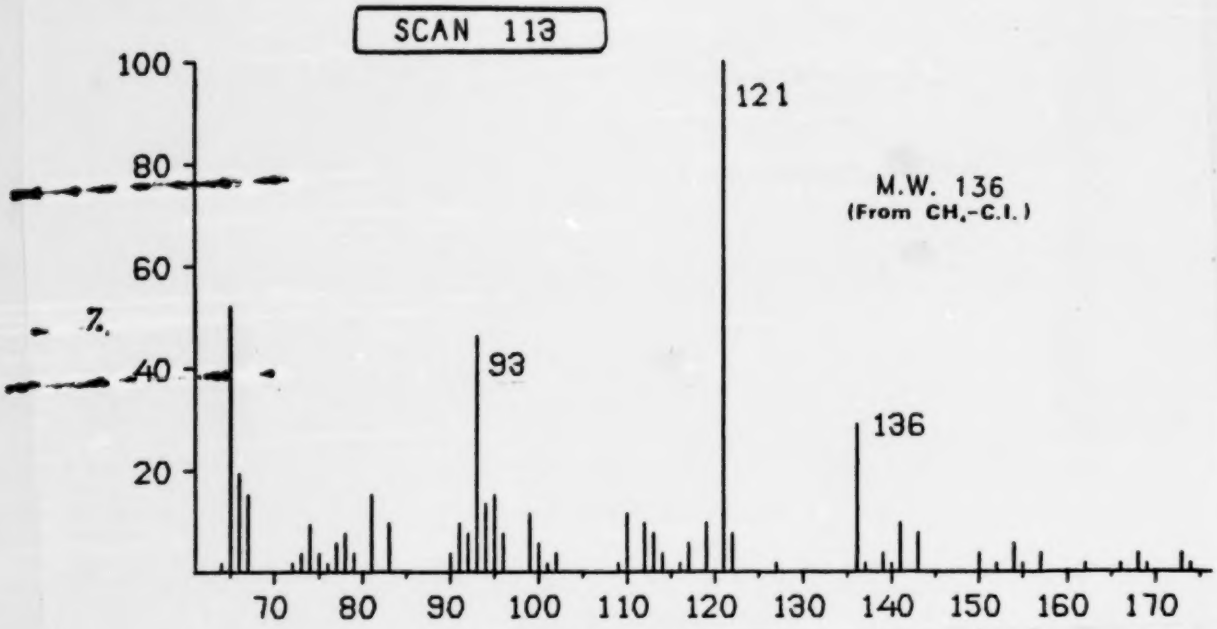

Figure 6. Electron impact mass spectrum of Scan 113.